

Cumulant expansion for ferrimagnetic spin (S_1, s_2) systems

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We have generalized the application of cumulant expansion to ferrimagnetic systems of large spins. We have derived the effective Hamiltonian in terms of classical variables for a quantum ferrimagnet of large spins. A noninteracting gas of ferrimagnetic molecules is studied systematically by cumulant expansion to second order of (Js/T) where J is the exchange coupling in each molecule, s is the smaller spin (S_1, s_2) and T is temperature. We have observed fairly good results in the convergent regime of the expansion, i.e $T > Js$. We then extend our approach to a system of interacting ferrimagnetic molecules. For one dimensional nearest neighbor interaction we have observed that the correlation of more than two neighboring sites is negligible at moderate and high temperature behavior. Thus the results of a single molecule can be applied to the chain of interacting molecules for temperatures greater than classical energy scale, i.e $T > JS_1s_2$. Finally we will discuss the effect of spin inhomogeneity on the accuracy of this method.

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I. INTRODUCTION

Ferrimagnets are systems composed of different spins, mostly of two types $(S_1, s_2)^{1,2}$. Many of ferromagnetic materials are essentially ferrimagnets³. It is a special class of spin models with much attraction in low dimension where their universality class is completely different from homogeneous spin models⁴. Antiferromagnetic chain of spin s models are gapless (gapped) for half-integer (integer) spins⁵. However ferrimagnetic chains behave differently. The low energy spectrum of a ferrimagnetic chain $(1, 1/2)$ is gapless with ferromagnetic order and a gapped band above it which has antiferromagnetic properties^{6,7}. This effect causes a crossover from ferromagnetic to antiferromagnetic behavior at finite temperatures^{8,9}.

Spin wave theory gives an explanation for low temperature physics of ferrimagnetic chains¹⁰. However, it is valid for temperatures smaller than the classical energy scale ($T \lesssim JS_1s_2$). It is our task to obtain the physics of ferrimagnets systematically at moderate (where quantum corrections are important) and higher temperatures. Cumulant expansion (CE)^{11,12,13} is our approach to this problem. Recently this approach has been implemented to study finite temperature behavior of homogeneous large spin systems^{14,15}. It has been observed that cumulant expansion converges in a region $T > Js$ which is wider than corresponding one in the high temperature series expansion and even overlaps the validity regime of spin wave theory for homogeneous spin systems.

We have generalized the application of cumulant expansion to ferrimagnetic models. In this approach we obtain a quasiclassical Hamiltonian for a (S_1, s_2) system. The effective Hamiltonian which is a function of classical variables takes into account the quantum corrections systematically in the order of (Js/T) where s is the smaller value of (S_1, s_2) . The partition function is calculated by using the effective Hamiltonian to get physical properties. Apart from the effective Hamiltonian for a general

(S_1, s_2) ferrimagnets we found that the n -th order effective Hamiltonian contains correlation of $(n + 2)$ -sites. Moreover, for nearest neighbor interaction in ferrimagnetic chain, the first order effective Hamiltonian is composed of 2-sites correlation. Consequently the results of CE for a single molecule of (S_1, s_2) is the same as one dimensional interacting molecules. We have also found that in the convergence region, the gas model is a good representation of a chain of interacting molecules up to 2nd order expansion.

It is remarkable that in the special case $S_1 = s_2$, our results match the recent studies on homogeneous spin chains^{14,15}.

The outline of this paper is as follows. In section II we have introduced the cumulant expansion in spin coherent state representation. The effective Hamiltonian and partition function of two sites gas model are derived in sec. III. In section IV we have derived the effective Hamiltonian of ferrimagnetic chain and then the physical properties. Results and discussion have been demonstrated in sec.V where we have presented some physical quantities of a chain with nearest neighbor interaction.

II. CUMULANT EXPANSION IN SPIN COHERENT STATE REPRESENTATION

The cumulant of N operators or classical variables (A_i) is defined as^{11,12}

$$\begin{aligned} & \langle A_1 \dots A_n \rangle^c \\ &= \frac{\partial}{\partial \lambda_1} \dots \frac{\partial}{\partial \lambda_n} \ln \langle e^{\lambda_1 A_1 + \lambda_2 A_2 + \dots} \rangle |_{\lambda_1 = \dots = \lambda_n = 0} \end{aligned} \quad (2.1)$$

where $\langle \dots \rangle$ means averaging over a classical distribution function or a quantum state¹². It is easy to show that in case of all A_i equal to A , one will arrive at the following equality,

$$\ln \langle e^{\lambda A} \rangle = \langle e^{\lambda A} - 1 \rangle^c. \quad (2.2)$$

To do so, multiplying by $\lambda^n/n!$ and summing over $n = 1, 2, \dots, \infty$ is performed. Let us show the cumulant of few cases in terms of usual averaging.

$$\begin{aligned} \langle A \rangle^c &= \langle A \rangle, & \langle A_1 A_2 \rangle^c &= \langle A_1 A_2 \rangle - \langle A_1 \rangle \langle A_2 \rangle \\ \langle A_1 A_2 A_3 \rangle^c &= \langle A_1 A_2 A_3 \rangle - \langle A_1 \rangle \langle A_2 A_3 \rangle^c - \langle A_2 \rangle \langle A_1 A_3 \rangle^c \\ &\quad - \langle A_3 \rangle \langle A_1 A_2 \rangle^c - \langle A_1 \rangle \langle A_2 \rangle \langle A_3 \rangle \end{aligned} \quad (2.3)$$

It is obvious from Eq.(2.3) that the cumulant of two or more operator contains correlations of them. It is a characteristic property of quantum mechanics that the expectation value of a product of two operators is different from the product of expectation values ($\langle A_1 A_2 \rangle - \langle A_1 \rangle \langle A_2 \rangle \neq 0$, whereas the equality is valid in classical limit). This is the correlation of two operators which is inherited from the quantum state in which the expectation is calculated. So we expect to obtain a quasiclassical description by using cumulants. In this respect we are going to obtain an effective (quasiclassical) Hamiltonian in terms of cumulants which contain quantum corrections.

The partition function (Z) of a spin system can be expressed in the basis of spin coherent states $|\mathbf{n}\rangle$; i.e. states with the maximum-spin projection on the axis pointing in the direction of unit vector \mathbf{n} [18]. The basis of coherent states are overcomplete, so it contains all quantum states. The classical state of a spin is achieved in the limit $S \rightarrow \infty$. The unity operator in this representation is

$$\mathbf{1} = \frac{2S+1}{4\pi} \int d\mathbf{n} |\mathbf{n}\rangle \langle \mathbf{n}|. \quad (2.4)$$

The trace of an operator in a single spin problem can be written as:

$$\begin{aligned} \text{tr}(A) &= \sum_m \langle m|A|m \rangle = \frac{2S+1}{4\pi} \int d\mathbf{n} \sum_m \langle m|A|\mathbf{n}\rangle \langle \mathbf{n}|m \rangle \\ &= \frac{2S+1}{4\pi} \int d\mathbf{n} \langle \mathbf{n}|A|\mathbf{n} \rangle. \end{aligned} \quad (2.5)$$

So the partition function of a system of N -spins defined by the Hamiltonian \hat{H} , is as the following,

$$Z = \int \prod_{i=1}^N \left(\frac{2S_i+1}{4\pi} \right) d\mathbf{n}_i \langle \mathbf{n}_1 \cdots \mathbf{n}_N | e^{-\beta \hat{H}} | \mathbf{n}_1 \cdots \mathbf{n}_N \rangle \quad (2.6)$$

where $\beta = 1/T$ (choosing $k_B = 1$). If we define

$$e^{-\beta \mathcal{H}} \equiv \langle \mathbf{n}_1 \cdots \mathbf{n}_N | e^{-\beta \hat{H}} | \mathbf{n}_1 \cdots \mathbf{n}_N \rangle \quad (2.7)$$

then the partition function is the same as a classical one. Using Eq.(2.2), the effective Hamiltonian is expressed in terms of cumulants.

$$\beta \mathcal{H} = \langle \mathbf{n}_1 \cdots \mathbf{n}_N | 1 - e^{-\beta \hat{H}} | \mathbf{n}_1 \cdots \mathbf{n}_N \rangle^c \quad (2.8)$$

The above equation can be expanded in the following form by a Taylor expansion.

$$\begin{aligned} \beta \mathcal{H} &= \beta \langle \hat{H} \rangle^c - \frac{\beta^2}{2!} \langle \hat{H} \hat{H} \rangle^c + \frac{\beta^3}{3!} \langle \hat{H} \hat{H} \hat{H} \rangle^c + \dots \\ &= \beta (\mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \dots) \end{aligned} \quad (2.9)$$

TABLE I: The nonzero cumulants of $\langle (\mathbf{S}_1 \cdot \mathbf{s}_2)(\mathbf{S}_1 \cdot \mathbf{s}_2) \rangle^c$

X_1	x_2	X_3	x_4	$\langle (X_1 x_2)(X_3 x_4) \rangle^c$	
S_1^+	s_2^+	S_1^-	s_2^-	$\langle S_1^+ S_1^- \rangle^c \langle s_2^+ s_2^- \rangle^c$	$4\omega s^2$
S_1^+	s_2^z	S_1^-	s_2^z	$\langle S_1^+ S_1^- \rangle^c \langle s_2^z \rangle \langle s_2^z \rangle$	$2\omega s^3$
S_1^z	s_2^+	S_1^z	s_2^-	$\langle s_2^+ s_2^- \rangle^c \langle S_1^z \rangle^c \langle S_1^z \rangle$	$2\omega^2 s^3$

Thus the effective Hamiltonian (\mathcal{H}) can be considered as a systematic expansion in terms of cumulants of powers of \hat{H} . The first term ($\mathcal{H}^{(0)}$) is the pure classical contribution and higher orders are responsible for quantum corrections. In fact this is an expansion in powers of (Js/T) where s is the smaller spin of (S_1, s_2) in a ferrimagnetic chain, (it will be shown in next sections). This expansion is justified whenever $T > Js$. To the best of our knowledge, a high temperature expansion for mixed spin systems (S_1, s_2) is still missing in the literature. However to make a qualitative comparison we consider the homogeneous case^{14,15} ($S_1 = s_2 = S$). In this case the convergence region of CE; i.e $T > JS$, is larger than the typical high temperature expansion^{16,17} which is $T > JS^2$. As we will see in next sections CE can also be interpreted as an expansion of $1/s$. So for large spin ferrimagnets the range of convergence is wide.

III. TWO SITES GAS MODEL

Let us first consider an ideal gas-noninteracting-of ferrimagnetic molecules (gas model) where each molecule composed of two spins (S_1, s_2) . The interaction between spins in all molecules is either ferromagnetic or antiferromagnetic given by the following Hamiltonian.

$$\hat{H} = \mp JS_1 \cdot \mathbf{s}_2, \quad J > 0 \quad (3.1)$$

where \mathbf{S}_1 and \mathbf{s}_2 are spin operators of size S_1 and s_2 respectively. The $(-)$ sign stands for ferromagnetic (F) and $(+)$ for antiferromagnetic (AF) interaction. There are two reasons to study the gas model. Firstly, it is exactly solvable, so we will compare the results of cumulant expansion with the exact ones to infer the accuracy of our method. Secondly, we would like to address the connection of this model to a chain of interacting ferrimagnetic molecules (next section).

The eigenstates of Eq.(3.1) are labelled by total spin $S_t = |S_1 - s_2|, \dots, S_1 + s_2$. Each state is $2S_t + 1$ degenerate whose eigenvalue is $E_n = \mp \frac{J}{2} [S_t(S_t + 1) - S_1(S_1 + 1) - s_2(s_2 + 1)]$. In the incoming calculation of cumulants we define $s \equiv \min\{S_1, s_2\} = s_2$ and the following parameters,

$$\omega = \frac{S_1}{s_2} > 1, \quad \tilde{J} = Js^2. \quad (3.2)$$

In order to achieve the cumulants of Eq.(2.9) it is convenient to express the spin operator on each site in the coordinate system with the z axis along the coherent state

vector $\mathbf{n}_i \equiv \mathbf{n}_i^z$.

$$\mathbf{S}_i = \sum_{\alpha_i=z,\pm} \mathbf{n}_i^{\alpha_i} S_i^{\alpha_i}, \quad \mathbf{n}_{\pm} \equiv (\mathbf{n}_x \mp i\mathbf{n}_y)/2 \quad (3.3)$$

Where \mathbf{n}_x and \mathbf{n}_y are appropriate transverse basis vectors. Expanding $\langle \mathbf{S}_1 \cdot \mathbf{s}_2 \rangle$ in terms of spin components defined in Eq.(3.3) the only nonzero term in coherent state representation is $\langle (S_1^z \mathbf{n}_1) \cdot (s_2^z \mathbf{n}_2) \rangle = (\mathbf{n}_1 \cdot \mathbf{n}_2) \langle S_1^z s_2^z \rangle$. So the classical contribution to the effective Hamiltonian in Eq.(2.9) is: $\langle \hat{H} \rangle^c = \mp \tilde{J} \omega (\mathbf{n}_1 \cdot \mathbf{n}_2)$. Quantum corrections to the zeroth order approximation (classical) appear in the remaining terms. Keeping the first two corrections one should calculate the following expressions.

$$\langle \hat{H} \hat{H} \rangle^c = J^2 \langle (\mathbf{S}_1 \cdot \mathbf{s}_2) (\mathbf{S}_1 \cdot \mathbf{s}_2) \rangle^c \quad (3.4)$$

$$\langle \hat{H} \hat{H} \hat{H} \rangle^c = \mp J^3 \langle (\mathbf{S}_1 \cdot \mathbf{s}_2) (\mathbf{S}_1 \cdot \mathbf{s}_2) (\mathbf{S}_1 \cdot \mathbf{s}_2) \rangle^c \quad (3.5)$$

Using Eq.(3.3) there are 81 terms in $\langle \hat{H} \hat{H} \rangle^c$ among which three are nonzero. Table (I) shows the nonzero terms of four operators cumulant. A similar calculation has been done for $\langle \hat{H} \hat{H} \hat{H} \rangle^c$ to find the nonzero terms. In this case each cumulant contains the product of 6 operators where only 15 of them are nonzero. Summing up, we will arrive at the effective Hamiltonian up to second order corrections ($O(1/s^2)$). It is written in terms of classical variables where quantum effects has been considered.

$$\begin{aligned} \mathcal{H} = & \tilde{J} [\mp \omega (\mathbf{n}_1 \cdot \mathbf{n}_2) \\ & - \frac{1}{4} \left(\frac{\beta \tilde{J}}{s} \right) \omega (\omega + 1) (1 - (\mathbf{n}_1 \cdot \mathbf{n}_2)^2) \\ & - \frac{1}{8s} \left(\frac{\beta \tilde{J}}{s} \right) \omega (1 - \mathbf{n}_1 \cdot \mathbf{n}_2)^2 \\ & \mp \frac{1}{12} \left(\frac{\beta \tilde{J}}{s} \right)^2 (1 - (\mathbf{n}_1 \cdot \mathbf{n}_2)^2) \times \\ & (\omega^2 - (3\omega^2 + \omega^3 + \omega)(\mathbf{n}_1 \cdot \mathbf{n}_2))] \end{aligned} \quad (3.6)$$

The first term shows the classical contribution which simply represents the energy of coupled classical spins whose lengths are S_1 and s_2 . Quantum corrections have a non-Heisenberg form and their structure becomes more and more complex with increasing order. These corrections are important in the intermediate temperature where classical fluctuations are not strong enough to suppress quantum ones. At very high temperature the classical term is dominant. It is clear that Eq.(3.6) is an expansion in powers of $\beta \tilde{J}/s = Js/T$, so it is valid as far as $T > Js$.

To calculate the partition function we use Eqs.(2.6),(2.7) where \mathcal{H} comes from Eq.(3.6). Integration over spherical angles of \mathbf{n}_1 and \mathbf{n}_2 leads to the

following expression.

$$\begin{aligned} \ln Z = & \ln[(2\omega s + 1)(2s + 1)] + \ln \left(\frac{\sinh(\xi \omega)}{\xi \omega} \right) \\ & + \frac{B(1 + \omega)\xi}{2s} + \frac{1}{12s^2} (\mp B\omega\xi^2 - 3\omega\xi^2 + 15B\xi \\ & - 2\omega^2\xi^2 + 6B\omega\xi - 2\xi^2 \pm \frac{6B\xi}{\omega} + 3(1 + \omega)^2\xi^2 \\ & - \frac{9(1 + \omega)^2}{\omega} B\xi - \frac{3B^2\xi^2(1 + \omega)^2}{2}) \end{aligned} \quad (3.7)$$

where $\xi = \beta \tilde{J}$ and $B = \coth(\omega\xi) - 1/(\omega\xi)$ is the Langevin function. We can obtain the internal energy ($U = -\partial \ln Z / \partial \beta$) and heat capacity ($C = \partial U / \partial T$) in this approximation. Quasiclassical expansions for the internal energy and heat capacity of this model are shown in Figs.(1,2,3,4) for $(S_1, s_2) = (5/2, 2)$. They show how different contribution of classical, first and second order corrections sum up to the reasonable result. We have also plotted the exact solution of ferrimagnetic gas model for comparison. The corresponding values for ferrimagnetic chain of interacting molecules have been also plotted which will be discussed in next sections. In all of these plots the horizontal axis is scaled to dimensionless parameter $t = T/Js^2 = T/\tilde{J}$. Thus for large spins, it covers even the intermediate and low temperature regions. In the present case the convergence range of cumulant expansion reads to $t > 1/s = 1/2$.

A good agreement is observed between second order ($O(1/s^2)$) cumulant expansion and exact result for internal energy of F coupling which is shown in Fig.(1). For $t < 1/2$ it shows large deviation from exact result and diverges as $t \rightarrow 0$. The reason for divergence is as follows. The internal energy up to second order approximation ($O(1/s^2)$) would be,

$$\begin{aligned} \frac{U}{Js^2} = & -[\omega B + \frac{1 + \omega}{2s}(A\xi + B)] \\ & + \frac{1}{12s^2} [(\mp 2B\omega - 6\omega + 15A - 4\omega^2 + 6A\omega - 4 \\ & + \frac{6A}{\omega} + 6(1 + \omega)^2 - 9\frac{(1 + \omega)^2}{\omega} A - 3(1 + \omega)^2 B^2)\xi \\ & + (\mp A\omega - 3(1 + \omega)^2 BA)\xi^2 + 15B + 6B\omega + \frac{6B}{\omega} \\ & - 9\frac{(1 + \omega)^2}{\omega} B)] \end{aligned} \quad (3.8)$$

where $A = \partial B / \partial \xi$. As $T \rightarrow 0$, U diverges since $\xi \rightarrow \infty$. The coefficient of linear term in ξ comes from both $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$ where they cancel each other as $\xi \rightarrow \infty$. Whereas the quadratic term ξ^2 needs a contribution from $\mathcal{H}^{(3)}$ to be regular at $\xi \rightarrow \infty$, which is not present in second order approximation. The heat capacity for F coupling of ferrimagnetic molecule is shown in Fig.(2). The classical and first order expansion are far from the exact result, however the correction of second order term makes an agreement for $t > 1/2$.

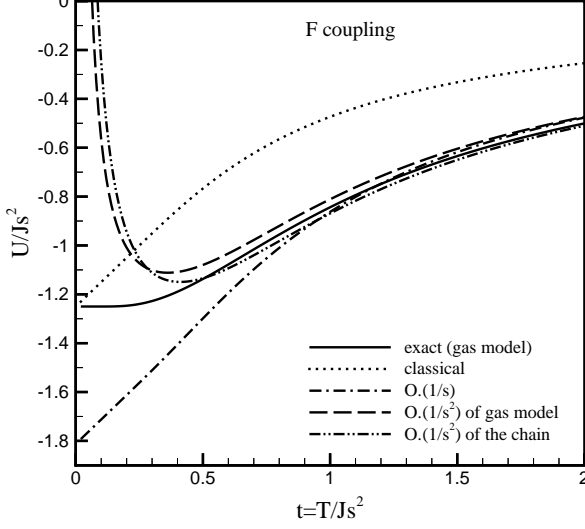


FIG. 1: Internal energy per molecule of the ferrimagnetic ($S_1 = 5/2, s_2 = 2$) gas model with ferromagnetic (F) coupling. Exact result of gas model (solid line) and different orders of cumulant expansion for gas model and chain of interacting molecules.

For AF coupling of gas model the normalized internal energy (U/\bar{J}) is plotted in Fig.(3). It is surprising that the second order expansion fits very well on the exact result even for very small values of t . A similar behavior can be seen in Fig.(4) for heat capacity. To understand the different behavior of cumulant expansion for F and AF coupling, let us come back to the energy levels. For F coupling the ground state has $S_t^{(0)} = (S_1 + s_2)$ and any excited state (E_n) can be obtained by $S_t^{(n)} = (S_1 + s_2) - n, n = 1, \dots, 2s_2, (S_1 > s_2)$. In the spectrum of F case the difference of energy levels ($\Delta E^{(l)} = E_l - E_{l-1} = JS_t^{(l-1)}$) decreases by increasing E_l . So it is like a quantum system. Where the converse is true for AF case. Moreover the absolute value of ΔE for the lowest states of F coupling is larger than AF case, i.e. $\Delta E^{(1)}(F) - \Delta E^{(1)}(AF) = J(2s_2 - 1)$. This means that cumulant expansion works better for AF case. In this respect we should note that a cumulant expansion similar to a high temperature series expansion starts from $T \rightarrow \infty$, where the probability of all states are equal. Then different order of expansion are responsible to recover the non-equal probability of states. This is crucial when the low energy spectrum is not dense (like F case) where a big difference exists between the occupation probability of lowest levels. Thus we expect to observe stronger quantum effects in the ferromagnetic case.

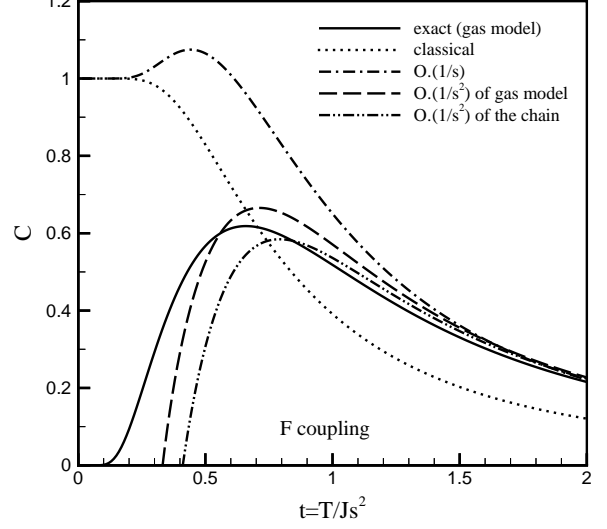


FIG. 2: The heat capacity per molecule of the ferrimagnetic ($S_1 = 5/2, s_2 = 2$) gas model with ferromagnetic (F) coupling. Exact result of gas model (solid line) and different orders of cumulant expansion for gas model and chain of interacting molecules.

IV. FERRIMAGNETIC SPIN CHAIN

We will now consider an interacting system of ferrimagnetic molecules. As it was noted in the introduction such systems can be synthesized to be considered effectively as one dimensional models (chains)^{1,2}, since the interchain coupling is very small compared to intra-chain ones. In this case the Hamiltonian of a ferrimagnetic chain of molecules is:

$$\hat{H} = \mp \sum_{i,j}^{\frac{N}{2}, \frac{N}{2}} J_{2i-1, 2j} \mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j} \quad (4.1)$$

It is supposed that larger spins (S) sit on the odd-numbered sites and smaller ones (s) on the even sites. The exchange coupling ($J_{2i-1, 2j}$) exists between any different spins. Our approach is general to cover long-range cases, however, later we will consider nearest neighbor coupling to obtain physical quantities.

To find an expansion for the physical quantities we should first calculate the semiclassical effective Hamiltonian defined in Eq.(2.9). Again, we will consider the cumulant expansion up to second order corrections of $1/s$ which comes from $\mathcal{H}^{(2)}$. Let us first calculate the classical term which is the simplest one.

$$\begin{aligned} \langle H \rangle^c &= \langle H \rangle = \mp \sum_{i,j} J_{2i-1, 2j} \langle \mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j} \rangle \\ &= \mp \omega \sum_{i,j} \tilde{J}_{2i-1, 2j} \mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j} \end{aligned} \quad (4.2)$$

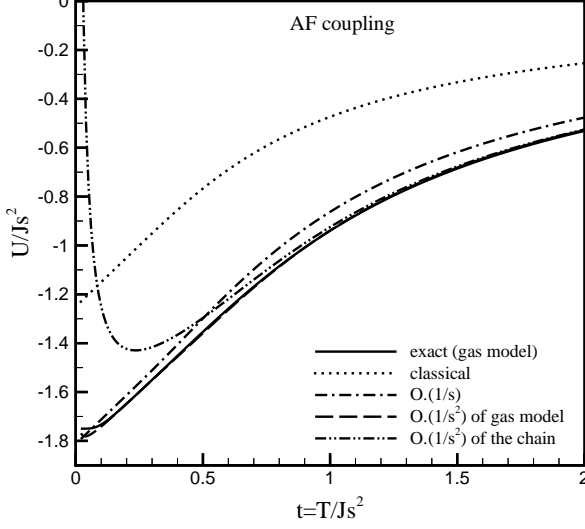


FIG. 3: Internal energy per molecule of the ferrimagnetic ($S_1 = 5/2, s_2 = 2$) gas model with antiferromagnetic (AF) coupling. Exact result of gas model (solid line) and different orders of cumulant expansion for gas model and chain of interacting molecules.

where as before $\tilde{J}_{2i-1,2j} = J_{2i-1,2j}s^2$ and Eq.(3.3) has been used. The first correction ($O(1/s)$) comes from the following term.

$$\langle HH \rangle^c = \sum_{i,j,l,k} J_{2i-1,2j} J_{2l-1,2k} \langle (\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2k}) \rangle^c \quad (4.3)$$

There are different sequences of i, j, l and k in $\langle (\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2k}) \rangle$ where indices can be in the same site, neighboring sites or apart from each other. We have summarized different cases in appendix which finally leads to the following result for $\mathcal{H}^{(1)}$.

$$\begin{aligned} \mathcal{H}^{(1)} = & \frac{-\beta\omega}{8s^2} \sum_{i,j} \tilde{J}_{2i-1,2j}^2 (1 - \mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})^2 \\ & - \frac{\beta\omega}{4s} \sum_{i,j,l} \tilde{J}_{2i-1,2j} \tilde{J}_{2i-1,2l} \times \\ & (\mathbf{n}_{2j} \cdot \mathbf{n}_{2l} - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})) \\ & - \frac{\beta\omega^2}{4s} \sum_{i,j,l} \tilde{J}_{2i-1,2j} \tilde{J}_{2l-1,2j} \times \\ & (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l-1} - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j})) \end{aligned} \quad (4.4)$$

As it is obvious from Eq.(4.4), the first correction which contains quantum effects is not of Heisenberg type. Moreover the second and third term in Eq.(4.4) contains coupled interaction of 3 sites, i.e. $(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})$

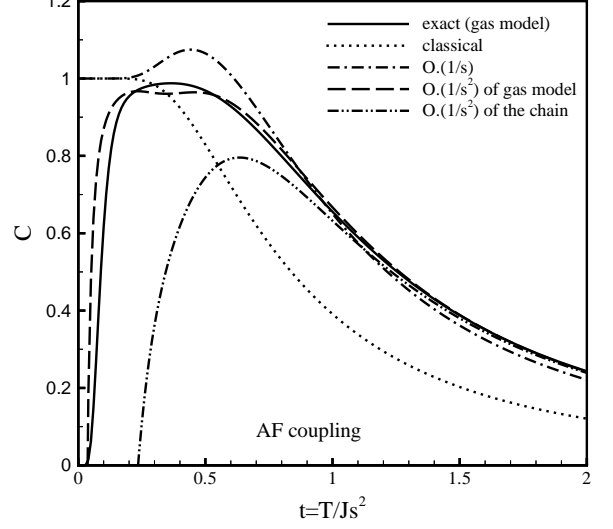


FIG. 4: The heat capacity per molecule of the ferrimagnetic ($S_1 = 5/2, s_2 = 2$) gas model with antiferromagnetic (AF) coupling. Exact result of gas model (solid line) and different orders of cumulant expansion for gas model and chain of interacting molecules.

and $(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j})$. This is different from two sites interaction of the original Hamiltonian, Eq.(4.1). It is the price of working with a classical Hamiltonian instead of the original quantum form. The last two terms of Eq.(4.4) give the information of 3 sites correlation. We will come back to this point later when comparing the results of gas model with a chain of interacting ferrimagnetic molecules. The third term of cumulant expansion is $\langle \hat{H} \hat{H} \hat{H} \rangle^c$, where the cumulant of 6 operators should be calculated. Each cumulant is composed of such terms, $\langle (\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2k})(\mathbf{S}_{2m-1} \cdot \mathbf{s}_{2n}) \rangle^c$. We have shown in appendix the different possible sequences of (i, j, l, k, m, n) which give nonzero cumulant. Summing up all nonzero cumulants, the second order semiclassical correction is

$$\begin{aligned} \mathcal{H}^{(2)} = & \mp \frac{\beta^2\omega^2}{4s^2} \sum_{i,j,l,k} \tilde{J}_{2i-1,2j} \tilde{J}_{2i-1,2l} \tilde{J}_{2k-1,2j} \Theta_1 \\ & \mp \frac{\omega\beta^2}{12s^2} \sum_{i,j,l,k} \tilde{J}_{2i-1,2j} \tilde{J}_{2i-1,2l} \tilde{J}_{2i-1,2k} \Theta_2 \\ & \mp \frac{\beta^2\omega^3}{12s^2} \sum_{i,j,l,k} \tilde{J}_{2i-1,2j} \tilde{J}_{2k-1,2j} \tilde{J}_{2l-1,2j} \Theta_3 \\ & \mp \frac{\beta^2\omega}{24s^3} \sum_{i,j,l} (\tilde{J}_{2i-1,2j}^2 \tilde{J}_{2i-1,2l} \Theta_4 + \omega \tilde{J}_{2i-1,2j}^2 \tilde{J}_{2l-1,2j} \Theta_5) \\ & \mp \frac{\omega}{24s^4} \sum_{i,j} \tilde{J}_{2i-1,2j}^3 \Theta_6 \end{aligned} \quad (4.5)$$

where Θ_i ; $i = 1, \dots, 6$ are defined below.

$$\begin{aligned}
\Theta_1 &= (\mathbf{n}_{2j} \cdot \mathbf{n}_{2k-1}) - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2k-1}) \\
&\quad - (\mathbf{n}_{2j} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2l}) \\
&\quad + (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2l}) \\
&\quad + \frac{1}{3}((\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2k-1})(\mathbf{n}_{2j} \cdot \mathbf{n}_{2l}) \\
&\quad - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2j} \cdot \mathbf{n}_{2k-1})), \\
\Theta_2 &= -4(\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2k}) \\
&= (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2k}) \\
&\quad - \frac{1}{3}[(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l} \cdot \mathbf{n}_{2k}) \\
&\quad + (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2j} \cdot \mathbf{n}_{2k}) \\
&\quad + (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2k})(\mathbf{n}_{2j} \cdot \mathbf{n}_{2l})], \\
\Theta_3 &= -4(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j}^-) \\
&= (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j}) \\
&\quad - \frac{1}{3}[(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2l-1}) \\
&\quad + (\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l-1}) \\
&\quad + (\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2k-1})], \\
\Theta_4 &= -\{(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(1 - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j}))^2 \\
&\quad + 2[(\mathbf{n}_{2j} \cdot \mathbf{n}_{2l}) + (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})^2(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l}) \\
&\quad - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2j} \cdot \mathbf{n}_{2l}) \\
&\quad - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})]\}, \\
\Theta_5 &= -\{(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j})(1 - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j}))^2 \\
&\quad + 2[(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l-1}) - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l-1}) \\
&\quad - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j}) \\
&\quad + (\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})^2]\}, \\
\Theta_6 &= (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(1 - (\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j}))^2. \tag{4.6}
\end{aligned}$$

Let us draw your attention to two properties of Eq.(4.5). If we factorize $\tilde{J} = Js^2$ from each term they are in $(\frac{\beta\tilde{J}}{s})^2$ order. However there are extra prefactors of powers of $(1/s)$ for some terms which make them less important for large s . This is a general property which is also valid for other orders of cumulant expansion. Generally, in the cumulant expansion the n -th order term, $\mathcal{H}^{(n)}$, can be considered of $\tilde{J}(\frac{\beta\tilde{J}}{s})^n$ order. The second point comes again from non-Heisenberg type of interaction in Θ_i . There are some terms which contain coupled interaction of 4 different sites, like $(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2l})$ in Θ_1 . Such terms give the information of 4-point correlation function. Thus the n -th order semiclassical Hamiltonian, $\mathcal{H}^{(n)}$, recovers the information of $(n+2)$ -sites correlation. However we found that for nearest neighbor interaction ($J_{i,j} = J\delta_{i,j\pm 1}$) the expectation value of $\mathcal{H}^{(1)}$ contains only nearest neighbor interaction. Thus, it contains the correlation of two sites the same as $\mathcal{H}^{(1)}$ for gas model. This means the first order approximation of ferrimagnetic gas model ($\mathcal{H}^{(0)} + \mathcal{H}^{(1)}$) would give the same approximation of first order one dimensional interacting molecules. This will be shown in next section.

V. RESULTS AND DISCUSSIONS

In this section we will present some physical quantities of a ferrimagnetic chain. Our results of previous section are general for any long-rang interaction of J_{ij} . However we consider nearest neighbor case, $J_{ij} = J\delta_{i,j\pm 1}$, to obtain internal energy and heat capacity. Because most of synthesized materials behave as nearest neighbor interacting molecules, moreover a comparison with other results is in this case.

Similar to the case of gas model the implementation of Eqs.(2.6) and (2.7) where \mathcal{H} is approximated by $\mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)}$ leads to

$$Z = \tilde{Z}_0[1 - \beta\langle\mathcal{H}^{(1)} + \mathcal{H}^{(2)}\rangle + \frac{\beta^2}{2!}\langle[\mathcal{H}^{(1)}]^2\rangle + \dots]$$

and

$$\begin{aligned}
\tilde{Z}_0 &= \left(\frac{2\omega s + 1}{4\pi}\right)^{\frac{N}{2}} \left(\frac{2s + 1}{4\pi}\right)^{\frac{N}{2}} Z_0, \\
Z_0 &= \int \prod_{i=1}^N dn_i e^{-\beta\mathcal{H}^{(0)}}.
\end{aligned}$$

To 2nd order approximation the partition function is

$$\begin{aligned}
Z &\cong (2\omega s + 1)^{\frac{N}{2}} (2s + 1)^{\frac{N}{2}} \left(\frac{\sinh(\omega\xi)}{\omega\xi}\right)^{N-1} \times \\
&\quad \left\{1 + N\left(\frac{\xi^2}{4s^2}(\omega \mp B\omega - \frac{B}{\xi}) + \frac{(1+\omega)B\xi}{2s}\right) \right. \\
&\quad + N\left[\frac{\xi^3}{4s^2}\left(\pm\frac{2B\omega}{3\xi} + \frac{6B}{\xi^2} - \frac{2\omega}{\xi}\right) \right. \\
&\quad + \frac{\xi^3}{6s^2}\left(-\frac{1}{\xi} + \frac{3B}{\omega\xi^2} - \frac{B^2}{\xi} - \frac{\omega^2}{\xi} + \frac{3B\omega}{\xi^2} - \frac{B^2\omega^2}{\xi}\right) \Big] \\
&\quad \left. + N\left(\frac{\xi^2}{8s^2}(1+\omega)^2\left(2 - \frac{6B}{\xi\omega} + NB^2\right) - \frac{\omega\xi^2B^2}{4s^2}\right)\right\}, \tag{5.1}
\end{aligned}$$

where we have used some integrals of Ref. [19]. Taking derivative of $\ln Z$ to β gives the internal energy

$$\begin{aligned}
\frac{U}{\tilde{J}} &\cong -\left\{\omega B + \frac{1+\omega}{2s}(A\xi + B) \right. \\
&\quad + \frac{1}{12s^2}[(2AB\xi^2 + 2B^2\xi)(-2 - 2\omega^2 - 3\omega) \\
&\quad + (A\xi + B)(15 + 6\omega + \frac{6}{\omega} - \frac{9}{\omega}(1+\omega)^2) \\
&\quad + 2\xi(-3\omega - 2 - 2\omega^2 + 3(1+\omega)^2) \\
&\quad \left. \mp \omega(A\xi^2 + 2B\xi)]\right\}. \tag{5.2}
\end{aligned}$$

That's simple to calculate the expression of heat capacity, $C = \partial U / \partial T$, which is not presented here.

We have plotted in Figs. (1, 3) the internal energy per molecule ($2U/N\tilde{J}$) of ($S_1 = 5/2, s_2 = 2$) ferrimagnetic

chain (--- line) for F and AF coupling respectively. As far as we know there is no other result for large spin systems to compare with. However we compare them with the corresponding values of different orders of gas model. We observe that the zero (classical) and first order expansion is the same for gas model and interacting chain. Because the 1st order expansion ($\mathcal{H}^{(0)} + \mathcal{H}^{(1)}$) contains information of two sites correlation. This can be shown easily by the following equation

$$\begin{aligned} \langle \mathcal{H}^{(1)} \rangle &= \frac{-\beta\omega\tilde{J}^2}{8s^2} \sum_{i=1}^N \langle (1 - \mathbf{n}_i \cdot \mathbf{n}_{i+1})^2 \rangle \\ &\quad - \frac{\beta\tilde{J}^3}{4s} \omega(\omega+1) \sum_{i=1}^N \langle 1 - (\mathbf{n}_i \cdot \mathbf{n}_{i+1})^2 \rangle. \end{aligned} \quad (5.3)$$

As far as the correlation of two sites is concerned the behavior of a single molecule and a chain of molecules with nearest neighbor interaction is the same. The inset of different behavior for chain and non-interacting molecules comes from the correlation of 3 sites. Such terms exist in $\mathcal{H}^{(2)}$ and contribute in $1/s^2$ correction. We see the difference by $1/s^2$ expansion in Fig.(1). This deviation is more clear for low temperature regime where quantum effects are important. But for temperatures greater than classical energy scale, $T > JS_1s_2$, there is a good agreement between gas model and ferrimagnetic chain. This shows that the correlation of more than two sites is important for low temperatures, $t < \omega$. In other words, at moderate and higher temperature an ideal gas of molecules represents a chain of ferrimagnets very well.

We have also plotted in Figs.(2) and (4) the heat capacity of ferrimagnetic chain for F and AF coupling respectively. Similar to the behavior of internal energy, the classical and 1st order ($1/s$) expansion gives the same results of gas model. The 2nd order correction ($1/s^2$) makes the difference between chain and single molecule. However a single molecule represents well the behavior of a chain. This justifies long range correlations can be neglected for moderate and high temperature regime of ferrimagnetic chain. This is in agreement with previous conclusion that we can replace the results of the gas model for a chain of interacting ferrimagnetic molecules where temperature is greater than classical energy scale, $t > \omega$.

Heat capacity of both Figs.(2, 4) decreases for high t which is the sign of antiferromagnetic behavior in the upper part of spectrum of a ferrimagnetic chain. We also see a Schottky-like peak in C which is the result of ferromagnetic to antiferromagnetic crossover. However this peak is in the region where cumulant expansion is not necessarily convergent. Then our plots for $t \lesssim 1$ might not be reliable, although we know from other arguments^{8,9} this peak exists.

To see the effect of spin inhomogeneity we have also considered the case of $S_1 = 4, s_2 = 2$ ($\omega = 2$) for both gas model and ferrimagnetic chain which have not plot-

ted here. As mentioned before the first order correction contains information of two sites correlation which makes no difference between gas model and a chain of interacting molecules. We have found that quantum effects are more pronounced for larger ω in F coupling both in the internal energy and heat capacity. The second order cumulant expansion of heat capacity for larger ω reaches the exact value for temperature higher than the case of Fig.(2). Although we expect a better agreement for lower temperature by increasing spin magnitude, this is not the case if we increase one of them. Specially for F coupling, increasing ω makes larger energy difference for lower levels which makes the situation worse.

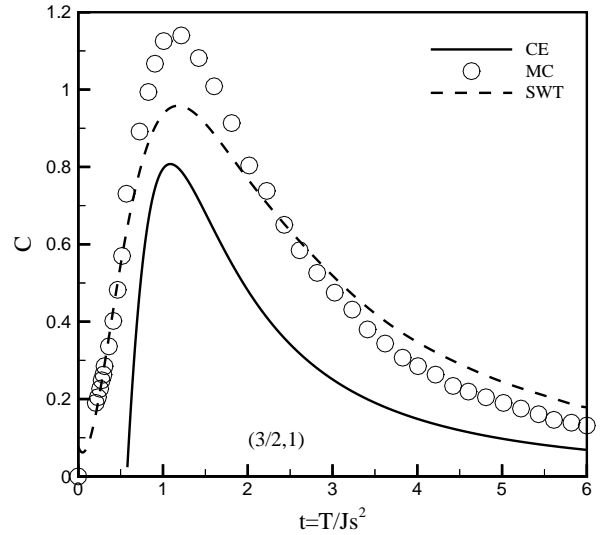


FIG. 5: Heat capacity per molecule of ferrimagnetic chain of $(3/2, 1)$ with AF coupling. Second order cumulant expansion (CE), Monte-Carlo (MC) simulation and spin wave theory (SWT).

For the AF coupling we have observed almost no different behavior comparing Figs.(3, 4) ($\omega = 5/4$) with the results of $\omega = 2$. In both groups, the second order cumulant expansion reaches the exact result of gas model at very low temperature. However this will not remain the same for large ω . We have increased ω to $S_1/s_2 = 7/2$ and observed good agreement for a little higher temperature. But still fairly well results of cumulants in the convergent region $t > 1/2$.

To the best of our knowledge there is no high temperature expansion for the thermodynamic properties of ferrimagnets in a closed form in the literature. The large S spin wave approximations^{2,9,20} are imposed to an extra constraint to be valid for moderate temperature. Because it is valid for low temperature (by definition) where only the low energy spectrum has the dominant effect. Adding an extra constraint needs a self consistent numerical solution to obtain thermodynamic properties. In comparison, our results are analytic (in a closed form) and general

in the sense that it can be applied to any ferrimagnetic system for arbitrary exchange couplings. The effective Hamiltonian derived here are in terms of arbitrary $J_{i,j}$ which covers long range interactions as well as any lattice structures.

However, we finally present the result of second order cumulant expansion (CE), spin wave theory (SWT) and Monte-Carlo (MC) simulation⁸ for heat capacity of ($S_1 = 3/2, s_2 = 1$) ferrimagnetic chain in Fig.(5). Although cumulant expansion is supposed to work well for large spin systems we present our results for (3/2, 1) ferrimagnets to compare with available results. The qualitative behavior of CE is the same as MC simulation but large deviation is observed for moderate temperature. The main reason for this deviation is the strong quantum nature of small spins. However, much better agreement is expected for larger spins.

As an out look, this work can be generalized to ladder geometry. It is known that the zero temperature behavior of ferrimagnetic ladders²¹ is different from homogeneous spin counterparts²². It is interesting to see the difference for finite temperature, for instance the evolution of magnetization plateaux^{23,24}.

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APPENDIX A: THE CUMULANT OF FOUR AND SIX OPERATORS FOR A SPIN CHAIN

In order to achieve the first order cumulant i.e. $\langle\langle(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2k})\rangle\rangle^c$, there are three nonzero sequences of i, j, l and k as follows

- Nonzero cumulant for $i = l$ and $j = k$. These are listed in table I
- For $i = l$ and $j \neq k$, the cumulant is $\langle\langle(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2j})\rangle\rangle^c$ and its value equals to $2\omega^2 s^3 (\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2l-1}^- \cdot \mathbf{n}_{2j}^-)$
- In the case of $j = k$ and $j \neq l$ the cumulant is $\langle\langle(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2k})\rangle\rangle^c$ which is equal to $2\omega s^3 (\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j}) (\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2l})$

In order to achieve the second order cumulant of the spin chain i.e. $\langle\langle(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2l-1} \cdot \mathbf{s}_{2k})(\mathbf{S}_{2m-1} \cdot \mathbf{s}_{2n})\rangle\rangle^c$, there are four nonzero sequences of i, j, l, k, m and n as follows

1. Three operators sit at a site and the others at another site, the cumulant is $\langle\langle(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})(\mathbf{S}_{2i-1} \cdot \mathbf{s}_{2j})\rangle\rangle^c$. There are only 15 different sequences which are nonzero.

TABLE II: Nonzero cumulant of six operators in a chain of interacting molecules (Eq.(4.1)). The first column shows the position of different spins. For instance 135, 24, 6 shows that X_1, X_3 and X_5 sit at a single site, x_2 and x_4 at the other site and x_6 sits at a separate one. $\langle A \rangle^c = \langle (X_1 x_2)(X_3 x_4)(X_5 x_6) \rangle^c$.

	X_1	x_2	X_3	x_4	X_5	x_6	$\langle A \rangle^c$
135, 24, 6	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^z	s_{2j}^-	S_{2i-1}^-	s_{2l}^z	$4\omega^2 s^4$
	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^+	s_{2j}^-	S_{2i-1}^-	s_{2l}^z	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^z	s_{2j}^-	S_{2i-1}^-	s_{2l}^z	$-4\omega s^3$
	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^z	s_{2j}^-	S_{2i-1}^-	s_{2l}^z	$-2\omega s^4$
135, 26, 4	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^-	s_{2l}^z	S_{2i-1}^z	s_{2j}^-	$\omega^2 s^4$
	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^+	s_{2l}^z	S_{2i-1}^-	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^z	s_{2l}^z	S_{2i-1}^-	s_{2j}^-	$-4\omega s^3$
	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^z	s_{2l}^z	S_{2i-1}^-	s_{2j}^-	$-2\omega s^4$
135, 46, 2	S_{2i-1}^+	s_{2l}^z	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^-	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2l}^z	S_{2i-1}^-	s_{2j}^+	S_{2i-1}^z	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2l}^z	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^-	s_{2j}^-	$-4\omega s^3$
	S_{2i-1}^z	s_{2l}^z	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^-	s_{2j}^-	$-2\omega s^4$
246, 13, 5	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^-	s_{2j}^z	S_{2k-1}^z	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^z	S_{2i-1}^-	s_{2j}^+	S_{2k-1}^z	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^+	S_{2i-1}^-	s_{2j}^z	S_{2k-1}^z	s_{2j}^-	$-4\omega^2 s^3$
	S_{2i-1}^z	s_{2j}^+	S_{2i-1}^z	s_{2j}^z	S_{2k-1}^z	s_{2j}^-	$-2\omega^3 s^4$
246, 15, 3	S_{2i-1}^+	s_{2j}^+	S_{2k-1}^z	s_{2j}^-	S_{2i-1}^-	s_{2j}^z	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^z	S_{2k-1}^z	s_{2j}^+	S_{2i-1}^-	s_{2j}^-	$4\omega^2 s^4$
	S_{2i-1}^+	s_{2j}^+	S_{2k-1}^z	s_{2j}^z	S_{2i-1}^-	s_{2j}^-	$-4\omega^2 s^3$
	S_{2i-1}^z	s_{2j}^+	S_{2k-1}^z	s_{2j}^z	S_{2i-1}^-	s_{2j}^-	$-2\omega^3 s^4$
246, 35, 1	S_{2k-1}^z	s_{2j}^+	S_{2i-1}^+	s_{2j}^z	S_{2i-1}^-	s_{2j}^-	$4\omega^2 s^4$
	S_{2k-1}^z	s_{2j}^+	S_{2i-1}^+	s_{2j}^-	S_{2i-1}^-	s_{2j}^z	$4\omega^2 s^4$
	S_{2k-1}^z	s_{2j}^+	S_{2i-1}^+	s_{2j}^z	S_{2i-1}^-	s_{2j}^-	$-4\omega^2 s^3$
	S_{2k-1}^z	s_{2j}^+	S_{2i-1}^z	s_{2j}^z	S_{2i-1}^-	s_{2j}^-	$-2\omega^3 s^4$

2. Three operators sit at a site, two operators sit at another one and the sixth one sits at a separate site, the nonzero cumulants are listed in table II. At the first column of the table II, we can observe operators which can be placed at the same site, (i.e at the first four row of the table $i = l = k, j = l$ and $k \neq n$)

3. When two operators sit at a site, the another two at another site and the fifth and sixth one sit at two different sites, the cumulant results to

$$\begin{aligned}
& 4\omega^2 s^4 (2(\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2l})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j}^-) \\
& + (\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2l})(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j}^-) \\
& + 2(\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2l})(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2j}^-) \\
& + (\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j}^-)(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2l})) .
\end{aligned}$$

4. Finally, if three operators sit at a site and other ones sit at three different sites, then there are two nonzero terms as follows

- (a) If $i = l = m$, j , k and n are not equal, the value of cumulant is
 $-2\omega s^4(\mathbf{n}_{2i-1}^+ \cdot \mathbf{n}_{2j})(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2l})(\mathbf{n}_{2i-1}^- \cdot \mathbf{n}_{2k})$.
- (b) If $j = k = n$, i , l and m are not equal, the value of cumulant is

$$-2\omega^3 s^4(\mathbf{n}_{2i-1} \cdot \mathbf{n}_{2j}^+)(\mathbf{n}_{2k-1} \cdot \mathbf{n}_{2j})(\mathbf{n}_{2l-1} \cdot \mathbf{n}_{2j}^-).$$

Note that, the second order cumulant expansion is the sum of above mentioned cases.

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